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It was the purpose of the Symposium on Chemical Precursors to Ceramics to promote exchange of information among chemists and materials scientists engaged in studies related to the chemistry of materials. Participants were chosen to represent perspectives of industrial, academic, and National laboratories. Molecular Growth Pathways in Silica Sol Gel Processing, topics addressed included sol-gel processing and organometallic precursors.

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FINAL REPORT

SYMPOSIUM ON CHEMICAL PRECURSORS TO CERAMICS

Purpose

It was the purpose of the Symposium on Chemical Precursors to Ceramics to promote exchange of information among chemists and materials scientists engaged in studies related to the chemistry of materials.

Participants

In selecting participants for the Symposium, we sought individuals who we believe are bringing freshness of results and outlook to the area. The topic of chemistry related to ceramics had not received attention at an American Chemical Society meeting for three years. A number of people have recently undertaken projects in this area, and significant progress has been made. Participants were chosen to represent perspectives of industrial, academic, and National Laboratories.

Speakers in the main sessions of the Symposium were:

<u>Speaker</u>	<u>Affiliation</u>
R. T. Baker	Du Pont Co.
C. J. Brinker	Sandia National Laboratories
J. S. Haggerty*	Massachusetts Institute of Technology
R. H. Heistand II	Dow Chemical Co.
L. V. Interrante *	Rensselaer Polytechnic Institute
W. G. Klemperer*	University of Illinois
J. Livage*	Universite' Pierre et Marie Curie
T. J. Marks*	Northwestern University
S. J. Mc Lain	Du Pont Co.
L. G. Sneddon*	University of Pennsylvania
T. D. Tilley *	University of California, San Diego
P. T. Wolczanski*	Cornell University

* Recipient of Financial Support

Six postdoctoral students made presentations at a poster session associated with the Symposium. They were given small stipends to defray portions of their expenses. Their names and associations are:

Student	Advisor	Affiliation
William S. Rees*	D. Seyferth	Massachusetts Institute of Technology
Kirk E. Yeager	J. M. Burlitch	Cornell University
Hui Jung Wu,	L. V. Interrante	Rensselaer Polytechnic Institute
Zhiping Jiang	L. V. Interrante	Rensselaer Polytechnic Institute
William J. Hurley	L. V. Interrante	Rensselaer Polytechnic Institute
Donna Narsavage	L. V. Interrante	Rensselaer Polytechnic Institute

* Present affiliation, Department of Chemistry, Florida State University

Sources of Financial Support

Organizations contributing to the financial support of the Symposium were:

AFOSR
American Chemical Society
Dow Chemical Co.
Du Pont Co.

The contributors of financial support were acknowledged in the Introduction to the Symposium.

Summaries of Presentations

Short summaries of the papers presented at the main sessions of the Symposium are recorded below, together with some editorial comments by the Investigators. Abstracts supplied by the authors to the American Chemical Society are appended to the report. Except for abstracts, written accounts were not solicited from the authors.

Walter G. Klemperer.- "Molecular Growth Pathways in Silica Sol-Gel Processing."

A classical study in which techniques were developed for chromatographic separation and identification of compositions and structures of silanols formed early in the reactions of tetraalkoxy silicon compounds $\text{Si}(\text{OR})_4$ with water. With information on the functionality of individual species taking part in condensation polymerization of the silanols, the complexity of the polymer is able to be predicted and understood in terms of the Flory-Stockmayer theory of polymerization of polyfunctional molecules. The results provide information on the polymerization reaction at a level of understanding not previously available.

Jacques Livage.- "Molecular Engineering and Sol-Gel Chemistry."

A picture of the development of metal oxides during hydrolysis of both silicon and transition metal alkoxides was derived by application of physical and spectroscopic methods of analysis. Modification of the reactivity of the systems by substitution of alkoxide groups with carboxylic acid and beta-diketone ligands was discussed.

Leonard V. Interrante.- "Studies of Organometallic Precursors to Aluminum Nitride."

Organoaluminum routes to aluminum nitride were discussed. Studies on the kinetics and mechanism of formation of a precursor of aluminum nitride, Me_2AlNH_2 , from $\text{Me}_3\text{Al}:\text{NH}_3$ were presented. An important discovery is that the decomposition of $\text{Me}_3\text{Al}:\text{NH}_3$ is catalyzed by the product Me_2AlNH_2 .

T. Don Tilley.- "Catalytic Dehydrogenative Polymerization of Silanes to Polysilanes by Zirconocene and Hafnocene Catalysts. A New Polymerization Mechanism."

The mechanism of dehydrogenative polymerization of organosilanes RSiH_3 was elucidated by kinetic analyses of reactions catalyzed by model zirconium and hafnium catalysts. Sigma-bond metathesis reactions were shown to account for the initiation and

propagation reactions. This is the first study in which information has been obtained to support a mechanism of this type of polymerization reaction.

Larry G. Sneddon- "Polymeric and Molecular Precursors to Boron-Based Ceramics."

Several routes to boron nitride developed in Sneddon's laboratory were presented. The synthesis and polymerization of vinyl derivatives of borazine and pentaborane, and their conversion to BN was discussed. The dimethylsulfide adduct of BBr_3 is a very effective precursor of boron nitride films. Catalytic and non-catalytic methods of forming polymers of borazine were described. Studies are in progress to determine if this polymer is structurally related to liquid crystalline petroleum-based pitch, a precursor of structurally-oriented carbon fibers.

John Haggerty- "Models for Synthesizing High Quality Si, SiC and Si_3N_4 Powders under High Number Density Conditions."

Gas phase synthesis of SiC and Si_3N_4 using laser-assisted decomposition of silane was discussed. Following careful analysis of flow patterns of materials in the reactor, silicon, silicon carbide and silicon nitride powders of controlled size and uniform particle size distribution were obtained. It was found useful to first grow particles of elemental silicon, and to coalesce these particles in the liquid state. Well-formed particles of silicon are then converted to the carbide or nitride. By running the reactor under conditions where molten silicon particles collide and coalesce to the desired size, high throughput is achieved.

C. Jeffrey Brinker- "Silicate Precursors to Sol-Gel Films and Fibers: Structure-Property Relationships."

Dr. Brinker was one of the primary representatives of the materials science community at this Symposium, and was asked to include general background information on sol-gel chemistry and structures in his talk. He presented a short tutorial on sol-gel

chemistry and structures, and showed how the principles applied to the formation of dense thin films of SiO_2 .

Robert H. Heistand II- "Chemical Precursors to Ceramics: A Chemical Process Viewpoint."

The use of organozinc compounds as precursors of zinc oxide, and catechol complexes of titanium as precursors of barium titanate were described. Stages of development of processes from laboratory to semiworks scales were discussed.

Tobin J. Marks- "Metal-Organic Chemical Vapor Deposition Routes to High- T_c Superconductors."

It was shown that easily available, volatile β -diketonate complexes can be supplied to a reactor in the gas phase and combined on a hot substrate to form superconducting films of good quality. The phases $\text{YBa}_2\text{Cu}_3\text{O}_x$; $(\text{BiO})_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$; and $(\text{TlO})_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ were prepared. Phase pure, crystalline and oriented films on a variety of substrates were obtained. T_c 's of the films approach the best reported for the respective bulk superconductors.

Stephan J. Mc Lain- "Solution Routes for the Preparation of Superconductor Powders and Fibers."

The synthesis of new copper alkoxides formed the basis for new routes to fibers and powders of the 123 superconductor. conclusions are:

- New Cu(II) alkoxides with γ -O or N atoms such as $\text{Cu}(\text{OCH}_2\text{CH}_2\text{OBu})_2$ and $\text{Cu}(\text{OCH}_2\text{CH}_2\text{NEt}_2)_2$ are soluble and can be used in solution routes to the 123 superconductor.
- Controlled hydrolysis of a solution of Y, Ba, and Cu complexes in tetrahydrofuran solution produces a carbon-free mixture of amorphous metal oxides.
- Firing this carbon-free precursor in argon allows the synthesis of 123 at temperatures near 650°C .
- The resulting 123 powder consists of aggregates of sub-micron particles with a narrow size distribution.

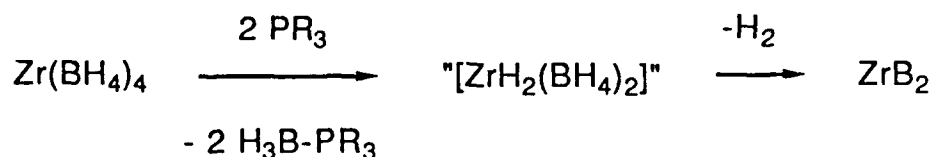
- Sintering of sub-micron 123 powder occurs near 925 °C to give large-grained dense bodies.

R. Thomas Baker- "Better Zirconium Boride Coatings through $\text{Zr}(\text{BH}_4)_4$ Chemistry,"

The preparation of zirconium boride coatings, ZrB_x , from the gas phase decomposition of $\text{Zr}(\text{BH}_4)_4$ at 200-400°C has been reported by a number of workers. While the ZrB_2 phase has been identified by powder X-ray diffraction, the B:Zr ratio of the bulk coatings varies with the experimental conditions and is usually greater than 2.5. Under conditions we have employed, the ratio is close to 3.8. Information on the decomposition mechanism has not been reported previously.

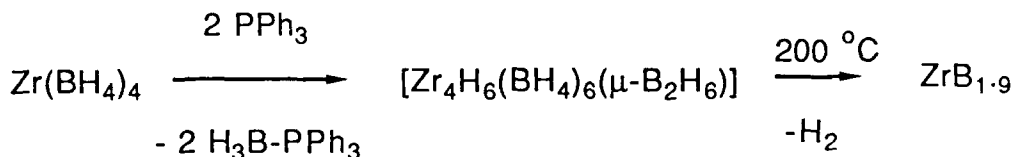
By studying the thermolysis of $\text{Zr}(\text{BH}_4)_4$ at 100°C we isolated in low yield a volatile intermediate characterized by NMR as $[\text{Zr}(\text{BH}_4)_3]_2(\mu\text{-B}_2\text{H}_6)$ with a bridging $(\text{B}_2\text{H}_6)^{2-}$ ligand resulting from the dehydrodimerization of Zr-coordinated $(\text{BH}_4)^{1-}$ ligands. The major thermolysis product is a black insoluble solid with the formula $\text{ZrB}_{3.8}\text{H}_x$ which is formulated as a mixture of oligomers resulting from the dehydrooligomerization of $\text{Zr}(\text{BH}_4)_4$. The consistency of the B:Zr ratio (near 4) throughout the several stages of decomposition shows that loss of hydrogen from zirconium borohydrides occurs preferentially to loss of boron hydrides under our conditions. It is suggested that competition between this pathway and one in which boron is lost by formation of volatile boron hydrides leads to the variations in the B:Zr ratio of coatings that have been reported in other work.

For ceramic composite applications, we wanted a solution route to ZrB_2 that would be suitable for coating large fiber bundles. We examined reactions of $\text{Zr}(\text{BH}_4)_4$ with Lewis bases with the goal of removing two BH_3 groups and forming bis(borohydride) zirconium hydride complexes, as illustrated in the idealized scheme below, where PR_3 represents tertiary phosphines.



Isolation and structural characterization of the new bis(chelate) complex, $\text{ZrH}_2(\text{BH}_4)_2(\text{DMPE})_2$ [DMPE = $(\text{Me}_2\text{PCH}_2)_2$], demonstrates the borane abstraction chemistry. Bulkier phosphine ligands give a

phosphorus-free precursor, thought to be a mixed-valent tetrazirconium cluster which also contains the bridging $(B_2H_6)^{2-}$ ligand, as characterized by 1H and ^{11}B NMR spectroscopy.



Heating this precursor above $200^\circ C$ gives black coatings of nearly stoichiometric zirconium diboride which may be heated to $1000^\circ C$ with no further weight loss.

Peter T. Wolczanski- "Polynuclear and Solid State Nitrides via Ammonolyses of Molecular Precursors."

New systems for formation of tantalum and zirconium nitride from neopentyl tantalum and -zirconium complexes are under development. Of special interest are proposed structures of intermediates in the ammonolysis of organotantalum compounds such as $Np_3Ta=CH^tBu$ (Np =neopentyl) where information has been obtained that traces evolution of the TaN structure from aminated organotantalum complexes. By use of this type of organometallic chemistry, a TaN phase difficult to obtain by solid state synthesis methods is easily achieved.

Treatment of $ZrNp_4$ or $Np_3Ta=CH^tBu$ with ammonia in benzene solution produces polymeric powders of high nitrogen content. Thermolysis of these powders leads to ZrN and TaN, respectively. Cubic ZrN forms at $700^\circ C$, well below temperatures ($1200^\circ C$) needed in conventional metal nitriding procedures conducted by exposing metal powder to molecular nitrogen or ammonia. TaN was also generated at a low temperature ($820^\circ C$, 1 atm). In this case, the low-temperature cubic phase was produced rather than the high-temperature hexagonal phase obtained by nitriding methods. Hexagonal TaN is less dense than cubic, which has been prepared under relatively extreme conditions, for example by heating hexagonal TaN at $1600^\circ C$ - $2000^\circ C$ at 5-100,000 atm. This discovery suggests that the intermediate powder contains structural elements similar to those found in the cubic TaN lattice. Preliminary

structural evidence pertaining to molecules formed prior to the polymeric precursor support the contention.

Parallels between molecular aggregates and solid state structures were also discovered. The exposure of CpTaMe_4 ($\text{Cp} = \eta^5\text{-C}_5\text{Me}_5$) to ammonia resulted in a cyclic nitride trimer, $(\text{CpMeTaN})_3$. The Ta_3N_3 ring of the trimer is akin to borazine and cyclic phosphazenes; the Ta-N linkages are equivalent and in the range of typical Ta=N bond distances. Molecular orbital calculations performed by Dr. Meinolf Kersting at Cornell revealed that an alternating-bond Kekule-like structure is disfavored. The structural characteristics of both the trimer and TaN are dominated by a localization of electron density on nitrogen.

This work is funded by the Air Force Office of Sponsored Programs and the Materials Science Center at Cornell.

APPENDIX

Authors' Abstracts (Main Sessions) of Presentations made at the Symposium on Chemical Precursors to Ceramics, American Chemical Society, Miami Beach, Florida, September 12, 1989.

85. MOLECULAR GROWTH PATHWAYS IN SILICA SOL-GEL PROCESSING.

W. G. Klemperer and Sangeeta Ramamurthi, Department of Chemistry and Materials Research Laboratory, University of Illinois at Urbana-Champaign, 505 South Mathews, Urbana, IL 61801.

Molecular weight and isomer distributions observed for low molecular weight polysilicate esters formed during the initial stages of tetramethylorthosilicate sol-gel polymerization are shown to be very sensitive to solution pH. These distributions are qualitatively consistent with entropy-controlled, Flory-Stockmayer molecular growth pathways with monomer functionalities of about two and four for acidic and basic reaction conditions, respectively. The implications of even higher monomer functionality can be probed using the cubic octamethyloctasilicate monomer. In this manner, the effect of precursor structure on the structure and properties of the resulting silica gel can be probed.

86. MOLECULAR ENGINEERING AND SOL-GEL CHEMISTRY. J. Livage, Chimie de la Matière Condensée, Université Pierre et Marie Curie, 4, place Jussieu Tour 54 - 5e etage, 75252 - Paris Cedex 05 France

Sol-gel chemistry is based on inorganic polymerization reactions. Oxide networks are synthesized via hydroxylation and condensation of molecular precursors. However, complexation by chemical species other than hydroxydes play an important role in the formation of condensed phases. Complexation leads to a chemical modification of the precursors at a molecular level changing both their functionality and reactivity. Taylor-made materials can therefore be made.

This paper presents an analysis of the role of complexation on the chemical reactions involved in the sol-gel process. Examples will be taken for both inorganic and metal-organic precursors.

87. STUDIES OF ORGANOMETALLIC PRECURSORS TO ALUMINUM NITRIDE. L. V. Interrante, F. Sauls, and Z. Jiang, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180-3590.

The pyrolytic conversion of various organoaluminum-nitrogen compounds and polymers have been studied in our laboratory as a potential source of AlN ceramics. These AlN precursors were derived from reactions of trialkylaluminum compounds with both ammonia and ethylenediamine and range from crystalline molecular solids to polymeric materials. Studies of the trimethylaluminum-ammonia system have included DSC measurements of the heats of reaction and kinetic studies of the "adduct"-to-"amide" conversion. In the case of the ethylenediamine system, both molecular and polymeric species have been identified by ^1H and ^{13}C NMR. The results of these studies, their implications with respect to the conversion of organoaluminum compounds to AlN, and the application of the various precursors to obtain AlN films and AlN/SiC/Si₃N₄ ceramics will be discussed.

88. CATALYTIC DEHYDROGENATIVE POLYMERIZATION OF SILANES TO POLYSILANES BY ZIRCONOCENE AND HAFNOCENE CATALYSTS. A NEW POLYMERIZATION MECHANISM. T. Don Tilley and Hee-Gweon Woo, Department of Chemistry, D-006, University of California, San Diego, La Jolla, CA 92093.

Polysilanes, $(-\text{SiRR}')_n$, represent a class of inorganic polymers that have unusual chemical properties and a number of potential applications. Currently the most practical synthesis is the Wurtz-type coupling of a dihalosilane with an alkali metal, which suffers from a number of limitations that discourage commercial development.

A coordination of polymerization route to polysilanes based on a transition metal catalyst offers a number of potential advantages. Both late and early metal dehydrogenative coupling catalysts have been reported, but the best to date appear to be based on titanocene and zirconocene derivatives. Our studies with transition metal silicon complexes have uncovered a number of observations that are relevant to this reaction chemistry, and hopefully important with respect to development of better catalysts. We have determined that many early transition metal silyl complexes are active catalysts for polysilane synthesis from monosilanes. A number of structure-reactivity correlations have been established, and reactivity studies have implicated a new metal-mediated polymerization mechanism. This mechanism, based on step growth of the polymer, has been tested in a number of ways. All proposed intermediates have now been observed in model reaction. Evidence for this mechanism will be presented.

89. POLYMERIC AND MOLECULAR PRECURSORS TO BORON-BASED CERAMICS. L. G. Sneddon, A. T. Lynch, J. S. Beck, W. Keller, and M. G. L. Mirabelli, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104.

As an alternative to high temperature processing techniques, there has recently been great interest in the development of polymeric precursors to boron ceramic materials. We report here the syntheses and ceramic conversion reactions of several new boron-containing polymer systems, including poly(vinylpentaborane), poly(vinyl-borazine) and poly(borazylene), as well as several related molecular complexes such as Lewis-Base borane adducts, which have been found to be high yield precursors to boron ceramics, including boron carbide and boron nitride. These molecular and polymeric materials can be made in high yields, are soluble in common organic solvents, and undergo controlled decompositions to ceramics at moderate temperatures. These properties have allowed the use of these precursors for the generation of thin-films, coatings and shaped ceramic materials.

90. MODELS FOR SYNTHESIZING HIGH QUALITY Si, SiC and Si₃N₄ POWDERS UNDER HIGH NUMBER DENSITY CONDITIONS. John S. Haggerty, Massachusetts Institute of Technology, Cambridge, MA 02139

High-number densities, needed to achieve acceptable manufacturing costs with small powders, present one of the greatest obstacles for achieving requisite qualities. At high temperatures, colliding particles tend to form aggregates that cause unacceptable defects in ceramic parts. Although CVD conditions have been defined by which uniform diameter particles can be grown in the absence of both sustained nucleation and interparticle collisions, low number densities and long exposure times give unacceptable mass flow rates.

We have developed a synthesis process for Si, SiC and Si₃N₄ powders based on growth proceeding by the collision and coalescence of liquid particles. Growth proceeds with decreasing number densities ($\sim 10^{12}$ - $10^{14} \rightarrow 10^9$ - 10^{10} cm^{-3}) for ~ 1 -20 ms

until the particles are quenched. Non-melting materials, like SiC and Si₃N₄, are formed by a 2-step process in which the nitriding and carbiding reactions are initiated after the molten Si particles have grown to final dimensions. The process model, the powder characteristics and the properties of the resulting parts will be discussed.

115. SILICATE PRECURSORS TO SOL-GEL FILMS & FIBERS: STRUCTURE PROPERTY RELATIONSHIPS. C. Jeffrey Brinker, R. A. Assink, G. C. Frye, A. J. Hurd, and K. J. Ward, Sandia National Laboratories, Albuquerque, NM 87185.

Depending on the synthesis conditions (pH, H₂O/OR, solvent, etc.), the structure of sol-gel silicates may be varied from weakly-branched, polymeric species characterized by a mass fractal dimension, $D \approx 2$, to highly branched clusters ($D = 2.4$), to fully-condensed, uniform (non-fractal) particles. These various species may be used as precursors to bulk, monolithic gels and glasses, thin films or fibers. We use ²⁹SiNMR and small angle x-ray scattering to investigate the local chemical structure and geometric structure on the ~1-20 nm length scales, respectively, both in the liquid and solid state. Adsorption studies and ellipsometry are used to investigate the porosity of deposited films and bulk xerogels. We find that under acidic conditions the polysilicate structures are consistent with random (statistical) irreversible cluster-cluster aggregation. For spinnable sols there is no evidence of linear or ordered, ladder polymers. The structures of base-catalyzed systems are more compact due to a continuous supply of monomers. Varying the precursor structure or the deposition conditions allow us to precisely tailor the porosity of films formed by dipping: volume fraction porosity (0-65%; average pore radius (<0.2 to 3 nm); surface area (1.2 to 316 m²/g).

116. CHEMICAL PRECURSORS TO CERAMICS: A CHEMICAL PROCESS VIEWPOINT. R.H. Heistand II, Ceramics & Advanced Materials, The Dow Chemical Company, 800 Building, Midland, Michigan 48667.

Numerous examples of fine ceramic powders and materials made from chemical precursors have been demonstrated in the laboratory in recent years. The duplication of these procedures during scale-up presents many challenges in the area of mixing, precipitation, filtration, washing and calcination. Illustrations of these problems from pilot plant experience on perovskites and other oxide ceramics will be presented. The ability to manufacture the desired fine ceramics depends upon the complete understanding of the process system. The goal of the presentation is to provide a process viewpoint for the basic research community to aid in the development of scalable chemical precursors to ceramics.

117. METAL-ORGANIC CHEMICAL VAPOR DEPOSITION ROUTES TO HIGH-T_c SUPERCONDUCTORS. Tobin J. Marks, Department of Chemistry and Materials Research Center, Northwestern University, Evanston, IL 60208-3113

If volatile molecular precursors and suitable gas-phase deposition chemistry can be developed, metal-organic chemical vapor deposition (MOCVD) offers an attractive approach to the synthesis of high-T_c superconducting thin films. Potential advantages vis-a-vis physical deposition techniques include greatly simplified apparatus, high deposition rates, amenability to coating complex shapes, tailorable film uniformity, adaptability to highly oxidizing deposition conditions, and the possibility of synthesizing metastable phases. This lecture describes the design and synthesis of volatile organometallic and coordination compounds for the formation of high-T_c superconducting

thin films by MOCVD. Combined with the appropriate methodologies for deposition and subsequent processing, highly oriented, phase pure thin films of the $\text{YBa}_2\text{Cu}_3\text{O}_x$, $(\text{BiO})_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$, and $(\text{TlO})_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ phases can be prepared. The structural and electrical properties of these films will be discussed.

118. SOLUTION ROUTES FOR THE PREPARATION OF SUPERCONDUCTOR POWDERS AND FIBERS. S. J. McLain, H. S. Horowitz, R. K. Bordia, and C.-H. Hsu, E. I. du Pont de Nemours & Co., Central Research and Development Department, Experimental Station, P. O. Box 80328, Wilmington, DE 19880-0328.

Our solution route to the 123 superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ begins with a homogeneous THF solution of $\text{Y}_5(\text{O})(\text{OCHMe}_2)_{13}$, $\text{Ba}(\text{OCHMe}_2)_2$, and either $[\text{Cu}(\text{NBu}_2)]_4$, or a soluble $\text{Cu}(\text{II})$ alkoxide. The solution of the metal complexes is hydrolyzed rapidly to produce a powder consisting of intimately mixed hydrated metal oxides. This carbon-free powder is converted to sub-micron superconducting 123 by firing in argon at 650°C , followed by reaction with O_2 at 400°C . The processing characteristics of this submicron powder will be discussed. The synthesis and characterization of new soluble $\text{Cu}(\text{II})$ alkoxides will also be described.

A new double alkoxide " $\text{Ba}_2\text{Y}(\text{OCH}_2\text{CH}_2\text{OEt})_7$ " can be used to prepare viscous fiber-forming solutions. Dense fibers of the 123 superconductor have been made by firing "green" fibers drawn from a mixture of 123 precursor powder suspended in a THF solution of $\text{Ba}_2\text{Y}(\text{OCH}_2\text{CH}_2\text{OEt})_7$ and a soluble $\text{Cu}(\text{II})$ complex.

119. BETTER ZIRCONIUM BORIDE COATINGS THROUGH $\text{Zr}(\text{BH}_4)_4$ CHEMISTRY. R. Tom Baker and Fred N. Tebbe, Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, DE 19880-0328.

Although the utility of $\text{Zr}(\text{BH}_4)_4$ as a synthon for zirconium boride ceramic coatings has been demonstrated by a number of workers, the mechanism of formation of the coatings is not understood and the stoichiometry of boride products is variable and poorly controlled. Initial studies on $\text{Zr}(\text{BH}_4)_4$ decomposition reactions have suggested reaction pathways and methods for the control of B:Zr ratios of the products. Conditions established for producing nearly stoichiometric ZrB_2 will be discussed.

120. POLYNUCLEAR AND SOLID STATE NITRIDES VIA AMMONOLYSES OF MOLECULAR PRECURSORS. Mark M. Banaszak Holl, Meinolf Kersting, Bradford D. Pendley and Peter T. Wolczanski, Cornell University, Baker Laboratory, Department of Chemistry, Ithaca, NY 14853.

Ammonolyses of $\text{Np}_3\text{Ta}=\text{CH}^i\text{Bu}$ (Np = neopentyl) resulted in the uptake of ~2.5 equiv of NH_3/Ta , the release of NpH and the precipitation of dark yellow/green powders. Analyses of typical batches were consistent with a " $\text{NpTa}_2\text{N}_5\text{H}_6$ " formulation. Thermolysis at 400°C resulted in a 20% weight loss and the formation of amorphous TaN , which could be annealed at 870°C to give cubic TaN . A similar sequence yielded cubic ZrN (700°C) from Np_4Zr . In a model system, ammonolysis of Cp^*TaMe_4 ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) generated a cyclic trimer of C_s symmetry, $[\text{Cp}^*\text{MeTaN}]_3$ (1). Trimer 1 possesses a nearly flat $[\text{TaN}]_3$ ring and equivalent TaN bond distances (1.886(17) Å ave.). These features are addressed via EHMO calculations. The complex also exhibits a reversible reduction at -2.01V (vs. Ag/AgCl) to the radical anion, $[\text{Cp}^*\text{MeTaN}]_3^-$ (1 $^-$), which can be synthesized as the potassium salt from NaK in THF. The theoretical and structural implications of 1 relative to solid nitrides will be discussed. Further

explorations concerning ammonolyses of bifunctional precursors will be presented. The structure of aggregates (clusters) intermediate between molecular and solid state compounds will be considered.